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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G03C 1/00, 1/725, 1/73, 1/735, 5/16, G03F 7/027, 7/038, 7/30	A1	(11) International Publication Number: WO 96/18133 (43) International Publication Date: 13 June 1996 (13.06.96)
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(54) Title: HIGH-RESOLUTION LETTERPRESS PRINTING PLATES AND WATER-SOLUBLE PHOTOPOLYMERIZABLE COMPOSITIONS COMPRISING A POLYVINYLALCOHOL DERIVATIVE USEFUL THEREFOR (57) Abstract In accordance with the present invention, water-developable photopolymerizable compositions useful for the preparation of durable printing plates capable of providing very high levels of resolution have been developed. Printing plates prepared employing invention compositions, once photopolymerized, have excellent physical properties, enabling their use in many very demanding applications, e.g., commercial letterpress and newspaper printing. Such applications require the photopolymerized resin to provide a sharp image and good durability after curing. Photopolymerization of invention resin yields a product with excellent physical characteristics, acceptable by letterpress printing standards. In addition, photopolymerization of invention composition provides a product which demonstrates sufficient toughness to be used for extended printing runs as required in such areas as metal decorating, newspaper, plastic packaging, business forms, and the like.		

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HIGH-RESOLUTION LETTERPRESS PRINTING PLATES AND WATER-SOLUBLE
PHOTOPOLYMERIZABLE COMPOSITIONS COMPRISING A POLYVINYLSOLUBLE
DERIVATIVE USEFUL THEREFOR

The present invention relates to water-developable photosensitive printing plates and compositions useful for the preparation thereof.

BACKGROUND OF THE INVENTION

5 Photosensitive resins used for the manufacture of relief printing plates are preferably developable with water rather than organic solvent. This is true for various reasons, such as ease of handling, health of workers who come in contact therewith, safety, and
10 avoidance of environmental pollution. Photosensitive resins used for the manufacture of relief printing plates must also be capable of providing a sharp, preferably durable image, especially when the desired end use is in letterpress applications.

15 Various photosensitive resins have been employed for the preparation of printing plates. The photosensitive resin compositions employed for conventional photosensitive resin plates are based on liquid unsaturated polyesters, polyvinyl alcohols, chemically modified polyvinyl alcohols,
20 water soluble polyamides, cellulose acetate succinates, alcohol soluble polyamides, etc. All these materials, however, suffer from disadvantages. For instance, liquid unsaturated polyesters are inconvenient to handle and necessitate the use of an alkaline solution or a special
25 air knife for developing. Cellulose acetate succinates require the use of an alkaline solution for development, and alcohol soluble polyamides typically require the use of an inflammable alcohol. Many chemically modified polyvinyl alcohols, after introduction of chemical modifying group(s)
30 thereto, require additional processing, e.g., isolation and/or purification steps, before the modified polymer can be incorporated into a photosensitive resin composition.

Numerous other water-developable, photopolymerizable compositions have been developed for the preparation of photosensitive resin plates. Each suffers from certain drawbacks, e.g., lack of sufficient structural integrity to withstand the physical rigors of commercial printing operations, requiring the use of expensive (exotic) raw materials (such as the base polymers employed for the preparation of such resins), and/or requiring the use of modified polymer systems which are expensive and time and labor intensive to prepare, and the like. Accordingly, what is still needed in the art are photopolymerizable resins having improved chemical and physical properties which can be prepared from readily available starting materials.

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BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention, we have developed novel water-developable photopolymerizable compositions useful for the preparation of durable printing plates capable of providing very high levels of resolution. Printing plates prepared employing invention compositions, once photopolymerized, have excellent physical properties, enabling their use in many very demanding commercial applications, e.g., commercial letterpress and newspaper printing. Such applications require the photopolymerized resin to provide a sharp image and good durability after curing. Photopolymerization of invention resin yields a product with excellent physical characteristics, acceptable by letterpress printing standards. In addition, photopolymerization of invention composition provides a product which demonstrates sufficient toughness to be used for extended printing runs as required in such areas as metal decorating, plastic packaging, newspaper printing, printing of business forms, and the like.

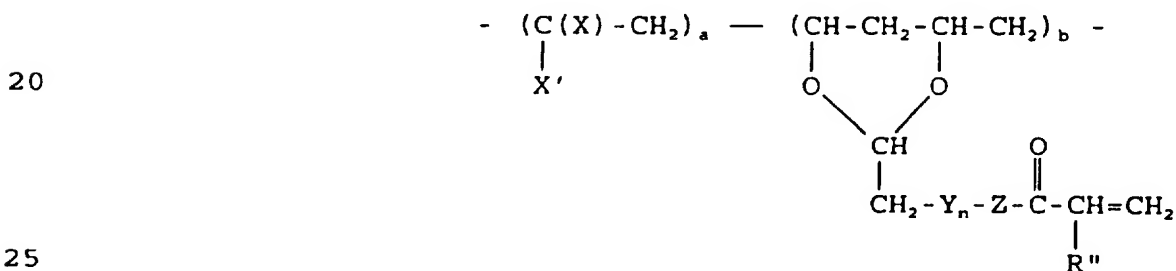
BRIEF DESCRIPTION OF THE FIGURES

Figure 1 illustrates the juncture between the face (top surface) and the shoulder of a character formed by photopolymerized polymeric compositions. Figure 1A illustrates the structure desired for a "sharp" image, while Figure 1B illustrates a structure which gives rise to a poorly defined image.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there are provided solid water-developable photopolymerizable compositions, which upon exposure to electromagnetic radiation form water insoluble polymer(s). Invention compositions comprise:

in the range of about 30 up to 75 wt % of a polymer system comprising a polyvinyl alcohol (PVA) derivative having the structure:



wherein:

X is hydrogen or -CO₂H,

X' is -OR, wherein each R is independently selected from -H, -CH₂CH₂OH or -C(O)CH₃, when X is hydrogen; or X' is -CH₂CO₂H when X is -CO₂H, with the proviso that at least 55 mol% of the X' groups are -OH;

each Y is independently selected from -CH₂- or -O-CH₂CH₂-;

each Z is independently selected from -O- or -NR'-, wherein each R' is independently selected from H or lower alkyl;

5 each R" is independently selected from H or lower alkyl;

a falls in the range of about 65 up to 99 mol%, based on the total moles of monomeric units contained in said PVA derivative (i.e., a+2b); and

10 b falls in the range of about 1 up to 35 mol%, based on the total moles of monomeric units contained in said PVA derivative, and

15 n falls in the range of about 0 up to 8,

in the range of about 1 up to 15 wt % aqueous medium,

20 in the range of about 10 up to 60 wt % of at least one ethylenically unsaturated monomer, and

in the range of about 0.1 up to 5 wt % of at least one photoinitiator,

wherein wt % in all instances is based on the
25 total weight of the composition.

Polymer systems contemplated for use in the practice of the present invention comprise a PVA derivative as defined above, optionally blended with substituted or unsubstituted polyvinyl alcohol (PVA). Where there is a
30 relatively low concentration of ethylenically unsaturated groups per ethylidene repeat unit of the above-described PVA derivative, the polymer system will typically contain little, if any, PVA "diluent"; while a substantial portion of the polymer system may comprise PVA as diluent where
35 there is a relatively high concentration of ethylenically

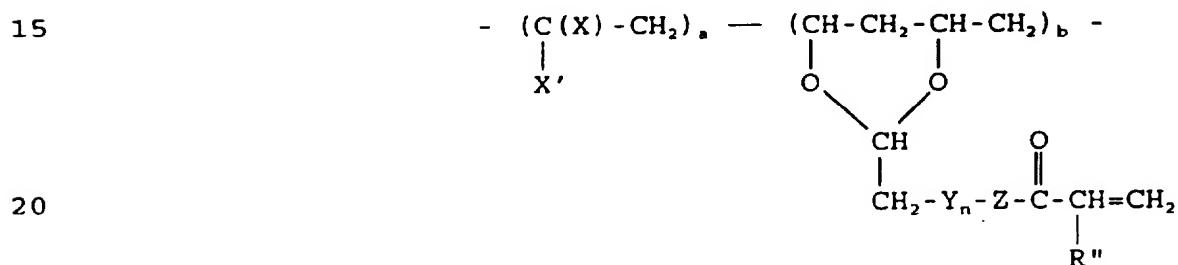
unsaturated groups per ethylidene repeat unit of the PVA derivative contemplated for use in the practice of the present invention. Typically, the mol % ethylenically unsaturated functionality present in the polymer system of the present invention will fall in the range of about 2 up to 25 mol %, based on the total moles of monomeric units contained in said PVA derivative (or in the PVA-based polymer system); with in the range of about 3 up to 15 mol % ethylenically unsaturated functionality in the polymer system preferred. It is presently especially preferred that the mol % of ethylenically unsaturated functionality in the polymer system employed in the practice of the present invention fall in the range of about 4 up to 9.

The desired concentration of ethylenically unsaturated functionality can be provided by a blend of the above-described PVA derivative with PVA, or by a PVA derivative as described above which directly provides the desired level of ethylenically unsaturated functionality. Since PVA derivatives as described above can readily be prepared having a wide range of ethylenic unsaturation content, blends containing various ratios of the above-described PVA derivatives and PVA can be prepared for use in the practice of the present invention.

As employed herein, "polyvinyl alcohol" refers to hydrolyzed polyvinyl acetate, having a degree of hydrolysis in the range of about 65 up to 98% (i.e., having about 65-98% free hydroxyl groups and 2-35% residual acetate groups). Preferably, polyvinyl alcohols having in the range of about 80-95% free hydroxyls will be employed. Polyvinyl alcohols having a wide range of molecular weights can be employed in the practice of the present invention. Polymeric species having a MW in the range of about 2,000 up to 100,000 are suitable, while presently preferred polymeric species will have a molecular weight in the range of about 5,000 to 50,000, with molecular weights in the

range of about 10,000 up to 30,000 being especially preferred. In addition, as recognized by those of skill in the art, PVAs employed in the practice of the present invention can be modified, for example, by ethoxylation
5 (see, for example, U.S. 4,272,611, incorporated by reference herein), by copolymerization of vinyl acetate with acrylates or methacrylates (for example, with itaconic acid), by copolymerization of vinyl acetate with vinyl amines (for example, vinylformamide), by esterification
10 with methacrylic anhydride (see, for example, U.S. 4,517,277, incorporated by reference herein), and the like.

PVA derivatives contemplated for use in the practice of the present invention are polymers having the structure:



wherein:

X is hydrogen or $-CO_2H$,

25 X' is -OR, wherein each R is
independently selected from -H, -CH₂CH₂OH or
-C(O)CH₃, when X is hydrogen; or X' is
-CH₂CO₂H when X is -CO₂H, with the proviso
that at least 55 mol% of the X' groups are
30 -OH;

each Y is independently selected from
-CH₂- or -O-CH₂CH₂-;

each Z is independently selected from
-O- or -NR'-, wherein each R' is
35 independently selected from H or lower
alkyl;

each R" is independently selected from H or lower alkyl;

5 a falls in the range of about 65 up to 99 mol%, based on the total moles of monomeric units contained in said PVA derivative (i.e., $a+2b$); and

10 b falls in the range of about 1 up to 35 mol%, based on the total moles of monomeric units contained in said PVA derivative.

Those of skill in the art recognize that the above-described PVA derivatives can be terminated in a variety of ways, e.g., by disproportionation, by recombination with reactive groups which are also present in the reaction
15 media, e.g., hydrogen radicals, methyl radicals, another growing polymeric chain, and the like. Preferred PVA derivatives contemplated for use in the practice of the present invention include those wherein X is hydrogen, X' is predominantly -OH (i.e., R is predominantly hydrogen),
20 Y is -CH₂-, Z is -O-, R" is hydrogen, a falls in the range of about 85 up to 97, b falls in the range of about 3 up to 15, and n falls in the range of about 0 up to 2. Especially preferred PVA derivatives contemplated for use in the practice of the present invention are those wherein:

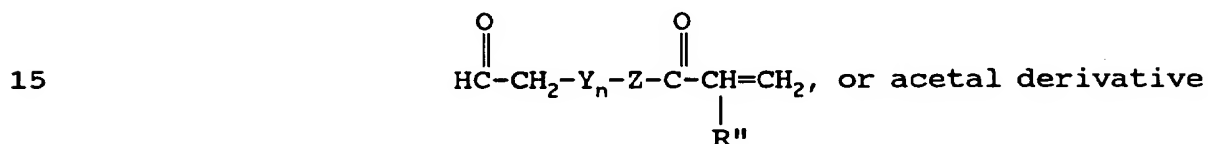
25 X is hydrogen, in the range of 70 up to 85 mol% of the X' groups are -OH, and in the range of 5 up to 25 mol% of the X' groups are -OAc, n is 0 (therefore Y is not present), Z is -NH-, R" is methyl, a falls in the range of 88 up to 98
30 mol%, and b falls in the range of 2 up to 12 mol%; or

35 X is hydrogen, in the range of 70 up to 85 mol% of the X' groups are -OH, and in the range of 5 up to 25 mol% of the X' groups are -OAc, Y is -CH₂- and n is 2, Z is -NH-, R" is methyl, a

falls in the range of 88 up to 98 mol%, and b falls in the range of 2 up to 12 mol%; or

5 X is hydrogen, in the range of 70 up to 85 mol% of the X' groups are -OH, and in the range of 5 up to 25 mol% of the X' groups are -OAc, n is 0, therefore Y is not present, Z is -O-, R" is methyl, a falls in the range of 88 up to 98 mol%, and b falls in the range of 2 up to 12 mol%.

10 The above-described PVA derivatives can be readily prepared by those of skill in the art. For example, polyvinyl alcohol can be contacted with at least one reactive species having the structure:



thereof, wherein R", Y, Z and n are as defined above. The above-described contacting is carried out in aqueous medium
20 under condensation conditions. Those of skill in the art can readily identify suitable condensation conditions, which typically comprise acidic media (e.g., pH \leq 3) and mild heating (i.e., temperatures in the range of about 60 up to 90°C).

25 Thus, for example, PVA can be condensed with a suitable reactive species (e.g., methacrylamido-butyraldehyde dimethyl acetal (MABDA), 2,2-dimethoxyethyl methacrylamide (DEMA), and the like) in the presence of a suitable acid (e.g., H₃PO₄, acidic ion exchange resin, and
30 the like). After the acid is neutralized and/or removed (e.g., by filtration to remove ion exchange resin), the resulting modified PVA can be mixed directly with the other components appropriate to produce the photopolymerizable composition of the invention.

As employed herein, the term "aqueous medium" contemplates water alone, as well as mixtures of water and organic media such as C₁ - C₄ alcohols (in a ratio anywhere from 1 part water per 10 parts alcohol up to 10 parts water per 1 part alcohol). Aqueous medium is typically employed in the range of about 1 up to 15 wt %; with media levels in the range of about 2-10 wt % being preferred; with 3-6 wt % aqueous media being presently preferred.

Typically, in the practice of the present invention, in the range of about 10 up to 60 wt % of at least one monomer is employed as part of the photopolymerizable composition. Preferably, in the range of about 20 up to 50 wt % monomer is employed, with in the range of about 35 up to 40 wt % being presently preferred.

As used herein, reference to "at least one monomer" embraces monounsaturated, monofunctional monomeric species, as well as unsaturated, polyfunctional monomeric species. As used herein, the term "monounsaturated, monofunctional monomeric species" refers to compounds having only one α,β -ethylenic site of unsaturation, and embraces a variety of acrylate and methacrylate compounds such as glycerol mono(meth)acrylate (i.e., glycerol monoacrylate or glycerol monomethacrylate), β -hydroxyethyl (meth)acrylate, β -hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, carboxyethyl acrylate (β -CEA), carboxyethyl methacrylate, dimethylaminopropyl (meth)acrylamide, and the like.

As used herein, the term "unsaturated, polyfunctional monomeric species", refers to compounds having more than one α,β -ethylenic site of unsaturation, and embraces such compounds as diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, glycerol di(meth)acrylate, epoxy

(meth)acrylates of glycols, aliphatic or aromatic urethane acrylates, and the like.

Those of skill in the art recognize that a wide range of photopolymerization initiators can be used in the practice of the present invention. As used herein, reference to "photoinitiator" embraces ordinary photoreaction initiators such as α -diketone compounds or monoketal derivatives thereof (e.g., diacetyl, benzil, benzil ketals, and the like), acyloins (e.g., benzoin, pivaloin, and the like), acyloin ethers (e.g., benzoin methyl ether, benzoin ethyl ether, benzoin propyl ether, benzoin vinyl ether, benzoin allyl ether, and the like), polynuclear quinones (anthraquinone, 1,4-naphthoquinone), benzophenone, hydroxy acetophenones, acyl phosphine oxides, and the like. Such compounds are typically employed at levels in the range of about 0.1 up to 3.0 wt %. Preferably, in the range of about 0.4 up to 2.3 wt % of initiator will be employed, with in the range of about 0.5 up to 1.0 presently preferred. The presently preferred initiator for use in the practice of the present invention is benzil dimethyl ketal.

Additional components contemplated for inclusion in the compositions of the invention include polymerization inhibitors (e.g., hydroxyaromatic compounds (e.g., hydroquinone, hydroquinone methyl ether (MEHQ; also known as p-methoxyphenol), p-t-butylcatechol, 2,6-di-t-butyl-p-cresol, pyrogallol, butylated hydroxytoluene (BHT), butylated hydroxyaniline (BHA), and the like); quinones (e.g., benzoquinone, p-toluquinone, p-xyloquinone, and the like); amines (e.g., N-phenyl- α -naphthylamine, and the like); imidazoles (e.g., methyl-benzimidazole); and the like); defoaming agents, surfactants, dyes, ultraviolet light absorbers, and the like. Invention compositions may also contain a plasticizer, which acts to reduce the glass transition temperature of the polymer, thereby improving

the flexibility of the resulting composition. Examples of plasticizers useful in the practice of the present invention include glycerin, ethoxylated phenols, ethoxylated glycerin, ethylene glycol, propylene glycol, and the like.

One of the desirable characteristics of invention compositions is their developability with water of substantially neutral pH. Thus, there is no need to use pH modified (i.e., acidic or basic) media when developing invention compositions. Another desirable characteristic of invention compositions is the high photosensitivity thereof, thus such resins require only a relatively short time for light exposure to accomplish the crosslinking thereof.

Invention compositions can be developed with water in 1 to 10 minutes or longer, depending on the water temperature, specific resin composition, resin thickness, and the like. Typically, invention compositions are developed for in the range of about 1 up to 5 minutes. After the resin is developed, it is dried in suitable fashion, optionally subjected to a post-cure exposure to strengthen the resin. Photocured and developed compositions can be used for printing immediately after drying and optional post-cure (which involves additional exposure of the dried plate to appropriate wavelength radiation for about 0.1 up to 20 minutes or longer).

In accordance with another embodiment of the present invention, there are provided solid water-developable photosensitive resin plates comprising a support having deposited thereon a layer of the above-described photopolymerizable composition. Invention resin plates are characterized by:

producing a sharp image, as determined by the method described in Example 2A, after photopolymerization and development thereof, producing an image capable of holding 2% dots at 120 lines per inch, as determined by the highlight dot holding test described in Example 2B, after photopolymerization and development thereof, being relatively insensitive to variations in processing conditions employed for washout of the photopolymerizable composition, and producing a durable printing surface after photopolymerization and development thereof.

Resin compositions of the present invention produce resin plates having the above-described excellent physical performance properties, while avoiding the need for high cost starting materials. Instead, invention compositions can be prepared from relatively low-cost, off-the-shelf starting materials (e.g., standard grade polyvinyl alcohol), and readily prepared ethylenically unsaturated derivatives thereof.

A "sharp image" (determined by the method described in Example 2A), after photopolymerization and development thereof refers to the profile of isolated dots and letters (referred to hereinafter as characters) on a developed plate. The juncture between the face (top surface) and the shoulder of the character is evaluated. The point where the character face meets the shoulder should be well defined, the face of the character dropping off crisply to the shoulder (as illustrated in Figure 1A). Unacceptable image sharpness is demonstrated by characters which are "rounded", i.e., the point where the character face meets the shoulder is not angular and well defined, but forms an arc (as illustrated in Figure 1B).

A particularly stringent test of image sharpness is the highlight dot holding test, wherein a high density grid of dot images is produced on a test plate, then observed to see how well the dot shape is retained after development of the plate. The finer the size of dots that can be retained, the greater the resolution which can be achieved. See Example 2B for a detailed description of how the highlight dot holding test is carried out. It is consistently observed that plates made with invention resin display improved dot holding properties, relative to plates made with prior art resins (see, for example, the Table presented following Example 1).

Another advantage of invention resins is the relative insensitivity of such resins to variations in processing conditions employed for washout of the photopolymerizable composition. Thus, invention compositions can be cured over a wide range of conditions (e.g., water temperature and wash times when developing the photopolymerized resins), without substantially affecting the properties of the resulting product.

Yet another advantage of invention resins is the production of a durable printing surface after photopolymerization and development thereof. Thus, invention compositions can be used in a variety of applications which entail long-term printing runs, high stress applications, and the like.

Supports contemplated for use in the practice of the present invention can be prepared of a variety of materials, e.g., metal, plastic, paper, wood, glass, and the like. Exemplary support materials include steel, aluminum and plastic (e.g., polyethylene terephthalate, Mylar, and the like).

"Depositing" of the above-described compositions onto support can be carried out in a variety of ways, e.g., by extrusion, roll coating, heat processing, solvent casting, and the like. These techniques can be readily
5 carried out by those of skill in the art.

The thickness of the layer of photopolymerizable composition applied in the preparation of invention photosensitive resin plates can vary widely. Typically, a resin thickness of at least 7 mils (i.e., 0.007 inches)
10 will be applied, with resin thickness of up to about 250 mils contemplated. Preferably, resin thicknesses in the range of about 5 up to 100 mils will be employed, with current commercial plates typically having a resin thickness in the range of about 10 up to 70 mils.

15 In accordance with a presently preferred aspect of the invention, an adhesive layer is applied to the support before the layer of photopolymerizable composition is deposited in the support. Suitable materials for use in preparing and applying such adhesive layers are well known
20 in the art. See, for example, United States Patent No. 3,360,746 (incorporated by reference herein), and the Examples which follow.

In accordance with another preferred aspect of the invention, a matte coat is applied on top of the layer
25 of photopolymerizable composition once said composition has been deposited on the support. Suitable materials for use in preparing and applying such matte coatings are well known in the art. See, for example, United States Patent No. 4,126,460, incorporated by reference herein, as well as
30 the Examples which follow.

In accordance with yet another embodiment of the present invention, there are provided relief printing plates comprising support having deposited thereon a

photopolymerized layer of photopolymerizable composition of the invention at a thickness of at least 7 mils. Invention printing plates are characterized as described above in terms of producing a sharp image, producing an
5 image capable of holding 2% dots at 120 lines per inch, being relatively insensitive to variations in processing conditions employed for washout of the photopolymerizable composition, and producing a durable printing surface after photo-polymerization and development thereof.

10 In accordance with another embodiment of the present invention, there is provided a method for preparing water-developable photosensitive relief printing plates, said method comprising depositing onto a suitable support a substantially homogeneous photopolymerizable composition
15 as described above at a thickness of at least 7 mils. The resulting plates are characterized as described above in terms of producing a sharp image, producing an image capable of holding 2% dots at 120 lines per inch, being relatively insensitive to variations in processing
20 conditions employed for washout of the photopolymerizable composition, and producing a durable printing surface after photo-polymerization and development thereof.

In accordance with yet another embodiment of the present invention, there is provided a method for preparing
25 a relief printing plate, said method comprising:

exposing a photosensitive resin plate as described above through a negative film having an image thereon to electromagnetic radiation of sufficient energy to promote the polymerization
30 of said resin, and

washing said plate with a sufficient quantity of water to remove the photosensitive resin composition from the non-exposed portions of said plate,

wherein said plate is characterized, after photopolymerization and development thereof, as described above in terms of producing a sharp image, producing an image capable of holding 2% dots at 120 lines per inch, being relatively insensitive to variations in processing conditions employed for washout of the photopolymerizable composition, and producing a durable printing surface.

The invention will now be described in greater detail by reference to the following non-limiting examples.

10

Example 1Preparation of Photopolymerizable CompositionsInvention Composition 1

100 parts by weight of a partially hydrolyzed polyvinyl alcohol having an average degree of polymerization of about 300 and a number average hydrolysis value of about 80 mol% were dissolved in 400 parts by weight of deionized water. Six (6) parts by weight of methacrylamidobutyraldehyde dimethyl acetal (MABDA) and 8.2 parts by weight of H_3PO_4 were added to the PVA solution. The mixture was stirred at about 70°C for about 3 hours. After 3 hours of stirring, the product was precipitated in acetone, then washed with acetone. The resulting PVA derivative was dried in a vacuum oven at about 50°C, then ground into a powder in a blender.

25

100 parts by weight of the PVA derivative prepared as described in the preceding paragraph were dissolved in 80 parts by weight of deionized water containing 0.006% of a dye (e.g., eosin) in a resin kettle. The components were heated to 85°C, then mixed for about 40 minutes. After mixing, 53 parts by weight of the following monomer solution were added, and the resulting combination mixed for several minutes (i.e., until the combination was substantially homogeneous):

30

29 parts 4-hydroxybutyl acrylate,
22 parts tetraethylene glycol diacrylate,
1.5 parts benzil dimethyl ketal,
0.4 parts butylated hydroxy toluene, and
5 0.1 parts hydroquinone monomethyl ether.

The resin composition was molded onto a coated steel support to a thickness of 20 mils (1 mil = 0.001 inch) using calender rolls, then dried (at ~80°C in a forced air oven) down to a residual water content in the
10 range of about 3-6 wt%. The coated steel support comprises a steel support having deposited thereon (for example, by roll coating) ~65 micron wet thickness of an adhesion layer of a composition containing pigment (for anti-reflectance), PVA, thickeners and latex adhesive. The dried resin film
15 on the coated steel support was then exposed to ultraviolet light provided by a fluorescent cold lamp through a negative mask. The negative was removed and the non-polymerized areas of the resin were washed out with plain water (i.e., water containing no additives). The resulting
20 relief plates were dried (at ~110°C for about 5 minutes), and then post-cured for about 5 minutes.

Evaluation of the relief images obtained showed that the shoulder angles were sharply defined (see Figure 1A), and 100% of the 2 mil highlight dots at 120 lpi were
25 held.

Comparative Composition A

The procedure employed for the preparation of Invention Composition 1 was repeated, except that 100 parts of a partially hydrolyzed polyvinyl alcohol having an
30 average degree of polymerization of 300 and number average degree of hydrolysis of about 80 mol% were substituted in place of the PVA derivative employed in the preparation of Invention Composition 1. The film was imaged and developed

as described above for the evaluation of Invention Composition 1.

Evaluation of the relief image showed that the shoulder angles were very rounded (see Figure 1B) and 0% of the 2 mil highlight dots at 120 lpi were held.

Invention Composition 2

45 parts by weight of a partially hydrolyzed polyvinyl alcohol having an average degree of polymerization of about 300 and a number average hydrolysis value of about 88 mol% were dissolved in 105 parts by weight of deionized water. 9 parts by weight of methacrylamidobutyraldehyde dimethyl acetal (MABDA) and 35 parts by weight of a solid phase acidic ion exchange resin (e.g., Amberlyst 15; available from Rohm & Haas, Philadelphia, PA) were added to the PVA solution. The mixture was stirred at about 70°C for about 6 hours. After 6 hours of stirring, the PVA derivative-containing solution was filtered using a 100 mesh filter screen.

106 parts by weight of the PVA derivative solution prepared as described in the preceding paragraph were added to a resin kettle containing 0.006% of a dye (e.g., eosin). 70 parts by weight of a partially hydrolyzed polyvinyl alcohol having an average degree of polymerization of about 300 and a number average hydrolysis value of about 80 mol% were added to the resin kettle. The components were then heated to 85°C, and then mixed for about 40 minutes. After mixing, 53 parts by weight of the following monomer solution were added, and the resulting combination mixed for several minutes (i.e., until the combination was substantially homogeneous)::

29 parts 4-hydroxybutyl acrylate,
22 parts tetraethylene glycol diacrylate,
1.5 parts benzil dimethyl ketal,
0.4 parts butylated hydroxy toluene, and

0.1 parts hydroquinone monomethyl ether.

The resin composition was molded onto a coated steel support to a thickness of 20 mils (1 mil = 0.001 inch) using calender rolls, then dried (at ~80°C in a forced air oven) down to a residual water content in the range of about 3-6 wt%. The coated steel support comprises a steel support having deposited thereon (for example, by roll coating) ~65 micron wet thickness of an adhesion layer of a composition containing pigment (for anti-reflectance), PVA, thickeners and latex adhesive. The dried resin film on the coated steel support was then exposed to ultraviolet light provided by a fluorescent cold lamp through a negative mask. The negative was removed and the non-polymerized areas of the resin were washed out with plain water (i.e., water containing no additives). The resulting relief plates were dried (at ~110°C for about 5 minutes), and then post-cured for about 5 minutes.

Evaluation of the relief images obtained showed that the shoulder angles were sharply defined (see Figure 1A), and 100% of the 2 mil highlight dots at 120 lpi were held.

Comparative Composition B

The procedure employed for the preparation of Invention Composition 2 was repeated, except that 100 parts of a partially hydrolyzed polyvinyl alcohol having an average degree of polymerization of 300 and number average degree of hydrolysis of about 80 mol% were substituted in place of the PVA derivative employed in the preparation of Invention Composition 2. In addition, 6 parts by weight of MABDA were added to the monomer solution. The film was imaged and developed as described above for the evaluation of Invention Compositions 1 and 2.

Evaluation of the relief image showed that the shoulder angles were rounded (see Figure 1B) and 0% of the 2 mil highlight dots at 120 lpi were held.

Invention Composition 3

5 100 parts by weight of a partially hydrolyzed polyvinyl alcohol having an average degree of polymerization of about 300 and a number average hydrolysis value of about 80 mol% were dissolved in 70 parts by weight of deionized water containing 0.006% of a dye (e.g., eosin)
10 in a resin kettle. 6 parts by weight of methacrylamido-butyr-aldehyde dimethyl acetal (MABDA) and 1.5 parts by weight of H_3PO_4 were added to the PVA solution. The mixture was stirred at about 85°C for about 40 minutes. After 40 minutes of stirring, 4.1 parts by weight of a 30% NaOH
15 solution were added to neutralize the acid, then 53 parts by weight of the following monomer solution were added, and the resulting combination mixed for several minutes (i.e., until the combination was substantially homogeneous):
29 parts 4-hydroxybutyl acrylate,
20 22 parts tetraethylene glycol diacrylate,
1.5 parts benzil dimethyl ketal,
0.4 parts butylated hydroxy toluene, and
0.1 parts hydroquinone monomethyl ether.

The resin composition was molded onto a coated
25 steel support to a thickness of 20 mils (1 mil = 0.001 inch) using calender rolls, then dried (at ~80°C in a forced air oven) down to a residual water content in the range of about 3-6 wt%. The coated steel support comprises a steel support having deposited thereon (for example, by
30 roll coating) ~65 micron wet thickness of an adhesion layer of a composition containing pigment (for anti-reflectance), PVA, thickeners and latex adhesive. The dried resin film on the coated steel support was then exposed to ultraviolet light provided by a fluorescent cold lamp through a
35 negative mask. The negative was removed and the non-

polymerized areas of the resin were washed out with plain water (i.e., water containing no additives). The resulting relief plates were dried (at ~110°C for about 5 minutes), and then post-cured for about 5 minutes.

- 5 Evaluation of the relief images obtained showed that the shoulder angles were sharply defined (see Figure 1A), and 100% of the 2 mil highlight dots at 120 lpi were held.

Comparative Composition C

- 10 The procedure employed for the preparation of Invention Composition 3 was repeated, except that no MABDA, no H_3PO_4 and no NaOH was added to the reaction mixture. The film was imaged and developed as described above for the evaluation of Invention Composition 1, 2 or 3.

- 15 Evaluation of the relief image showed that the shoulder angles were very rounded (see Figure 1B), and 0% of the 2 mil highlight dots at 120 lpi were held.

Invention Composition 4

- 20 100 parts by weight of a partially hydrolyzed polyvinyl alcohol having an average degree of polymerization of about 300 and a number average hydrolysis value of about 80 mol% were dissolved in 350 parts by weight of deionized water. To this, 7.25 parts by weight of 2,2-dimethoxyethyl methacrylamide (DEMA) and 58 parts by weight of a solid phase acidic ion exchange resin (e.g., Amberlyst 15) were added. The mixture was stirred at about 70°C for about 3 hours. After 3 hours of stirring, the product was precipitated in acetone, then washed with acetone. The resulting PVA derivative was dried in a vacuum oven at about 50°C, then ground into a powder in a blender.
- 30

- 100 parts by weight of the PVA derivative prepared as described in the preceding paragraph were dissolved in 63 parts by weight of deionized water containing 0.006% of a dye (e.g., eosin) in a resin kettle.
- 5 The components were heated to 85°C, then mixed for about 40 minutes. After mixing, 75 parts by weight of the following monomer solution were added, and the resulting combination mixed for several minutes (i.e., until the combination was substantially homogeneous):
- 10 35 parts 4-hydroxybutyl acrylate,
 20 parts tetraethylene glycol diacrylate,
 18 parts glycerol monomethacrylate,
 1.5 parts benzil dimethyl ketal,
 0.4 parts butylated hydroxy toluene, and
15 0.1 parts hydroquinone monomethyl ether.

- The resin composition was molded onto a coated steel support to a thickness of 20 mils (1 mil = 0.001 inch) using calender rolls, then dried (at ~80°C in a forced air oven) down to a residual water content in the
- 20 range of about 3-6 wt%. The coated steel support comprises a steel support having deposited thereon (for example, by roll coating) ~65 micron wet thickness of an adhesion layer of a composition containing pigment (for anti-reflectance), PVA, thickeners and latex adhesive. The dried resin film
- 25 on the coated steel support was then exposed to ultraviolet light provided by a fluorescent cold lamp through a negative mask. The negative was removed and the non-polymerized areas of the resin were washed out with plain water (i.e., water containing no additives). The resulting
- 30 relief plates were dried (at ~110°C for about 5 minutes), and then post-cured for about 5 minutes.

- Evaluation of the relief images obtained showed that the shoulder angles were sharply defined (see Figure 1A), and 98% of the 2 mil highlight dots at 120 lpi were
- 35 held.

Comparative Composition D

The procedure employed for the preparation of Invention Composition 4 was repeated, except that 100 parts of a partially hydrolyzed polyvinyl alcohol having an average degree of polymerization of 300 and number average degree of hydrolysis of about 80 mol% were substituted in place of the PVA derivative employed in the preparation of Invention Composition 4. The film was imaged and developed as described above for the evaluation of Invention Composition 1, 2, 3 or 4.

Evaluation of the relief image showed that the shoulder angles were somewhat rounded (see Figure 1B), and approximately 16% of the 2 mil highlight dots at 120 lpi were chipped or missing.

The results of the above evaluations are summarized in the following table.

TableSummary of Properties of Invention
and Comparative Compositions

	Image Sharpness	Percentage of 2 mil dots held (@120 lines per inch)
Invention Comp. 1	sharply defined	100
Comparative Comp. A	very poorly defined; rounded	None
Invention Comp. 2	sharply defined	100
Comparative Comp. B	very poorly defined; rounded	None
Invention Comp. 3	sharply defined	100
Comparative Comp. C	very poorly defined; rounded	None
Invention Comp. 4	sharply defined	98
Comparative Comp. D	poorly defined; somewhat rounded	84

Example 2Test Evaluation MethodsA. Image Sharpness Assessment

Image sharpness assessment is based on the appearance of the profile of letters and isolated dots on a developed plate, the letters and isolated dots being referred to hereinafter as characters. The juncture between the face (top surface) and the shoulder of the character is evaluated. The point where the character face meets the shoulder should be well defined, the face of the character dropping-off crisply to the shoulder (as illustrated in Figure 1A). Unacceptable image sharpness is demonstrated by characters which are "rounded", i.e., the

point where the character face meets the shoulder is not angular and well defined, but forms an arc (as illustrated in Figure 1B).

B. Highlight Dot Holding Assessment

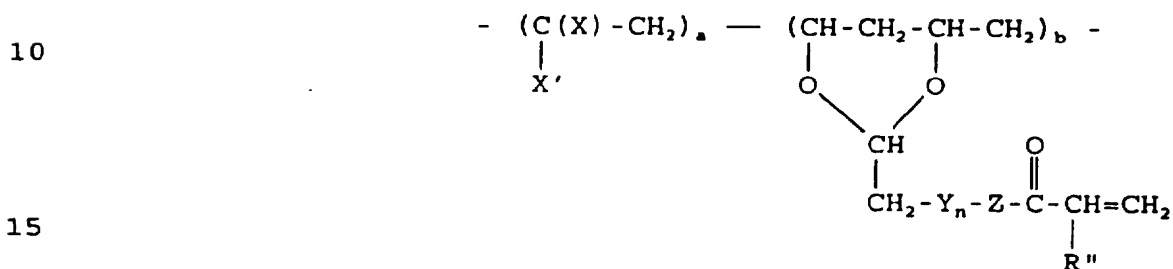
5 Highlight dot holding is assessed by inspection of the 2% 120 lines per inch (lpi) highlight dots with an optical microscope. The dots are viewed from directly above at 5X or 10X magnification, with the focus set for the top of the dots. The number of missing dots are then
10 manually counted, and the percent held calculated based on the total number of dots in the field of view. Four different regions of 2% highlight dots are viewed to ensure a representative accounting.

15 While the invention has been described in detail with reference to certain preferred embodiments thereof, it will be understood that modifications and variations are within the spirit and scope of that which is described and claimed.

That which is claimed is:

1. A solid water-developable photopolymerizable composition, which upon exposure to electromagnetic radiation forms a water insoluble polymer, said composition comprising

5 in the range of about 30 up to 75 wt % of a
 polymer system comprising a polyvinyl
 alcohol (PVA) derivative having the
 structure:



wherein:

X is hydrogen or $-CO_2H$,

20 X' is -OR, wherein each R is independently selected from -H, -CH₂CH₂OH or -C(O)CH₃, when X is hydrogen; or X' is -CH₂CO₂H when X is -CO₂H, with the proviso that at least 55 mol% of the X' groups are -OH;

25 each Y is independently selected from
 -CH₂- or -O-CH₂CH₂-;

each Z is independently selected from
-O- or -NR'-, wherein each R' is
independently selected from H or lower
alkyl;

each R" is independently selected from
H or lower alkyl;

35 a falls in the range of about 65 up to
 99 mol%, based on the total moles of
 monomeric units contained in said PVA
 derivative; and

b falls in the range of about 1 up to 35 mol%, based on the total moles of monomeric units contained in said PVA derivative, and
40 n falls in the range of about 0 up to 8,
in the range of about 1 up to 15 wt % aqueous medium,
45 in the range of about 10 up to 60 wt % of at least one ethylenically unsaturated monomer, and
in the range of about 0.1 up to 5 wt % of at least one photoinitiator,
50 wherein wt % in all instances is based on the total weight of the composition.

2. A composition according to claim 1 wherein said polymer system comprises
in the range of about 0 up to 95 wt % polyvinyl alcohol, and
5 in the range of about 5 up to 100 wt % of said PVA derivative.
3. A composition according to claim 1 wherein
a falls in the range of about 85 up to 97 mol%, and
b falls in the range of about 3 up to
5 15 mol%.
4. A composition according to claim 1 wherein the degree of polymerization of said PVA derivative falls in the range of about 200 up to 1500.
5. A composition according to claim 1 wherein said aqueous medium is water, and is present in the range of about 2 up to 8 wt %.

6. A composition according to claim 1 wherein said at least one ethylenically unsaturated monomer is a monounsaturated, monofunctional monomer, an unsaturated, polyfunctional monomer, or mixture thereof.

7. A composition according to claim 6 wherein said monomer comprises in the range of about 25-50 wt % of said composition.

8. A composition according to claim 6 wherein said monounsaturated, monofunctional monomer is selected from 4-hydroxybutyl (meth)acrylate, glycerol mono(meth)acrylate, β -hydroxyethyl (meth)acrylate, β -hydroxypropyl (meth)acrylate, carboxyethyl acrylate (β -CEA), carboxyethyl methacrylate, dimethylaminopropyl (meth)acrylamide, or combinations of any two or more thereof.

9. A composition according to claim 6 wherein said unsaturated, polyfunctional monomer is selected from diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, 5 tetraethylene glycol di(meth)acrylate, butane diol di(meth)acrylate, hexane diol di(meth)acrylate, neopentyl glycol di(meth)acrylate, glycerol di(meth)acrylate, epoxy (meth)acrylates of glycols, aliphatic urethane (meth)acrylates, aromatic urethane (meth)acrylates, or 10 mixtures of any two or more thereof.

10. A composition according to claim 1 wherein said photoinitiator is selected from α -diketone compounds or monoketal derivatives thereof, acyloins, acyloin ethers, polynuclear quinones, benzophenone, hydroxy acetophenones, 5 acyl phosphine oxides, or mixtures of any two or more thereof.

11. A composition according to claim 10 wherein said photoinitiator is present in the range of about 0.5 up to 2 wt %.

12. A composition according to claim 1 wherein X is hydrogen,
in the range of 70 up to 85 mol% of the X' groups are -OH, and in the range of 5 up to 25 mol% of the X' groups are -OAc,
n is 0, therefore Y is not present,
Z is -NH-,
R" is methyl,
a falls in the range of 88 up to 98 mol%,
and
b falls in the range of 2 up to 12 mol%.

13. A composition according to claim 1 wherein X is hydrogen,
in the range of 70 up to 85 mol% of the X' groups are -OH, and in the range of 5 up to 25 mol% of the X' groups are -OAc,
Y is -CH₂- and n is 2,
Z is -NH-,
R" is methyl,
a falls in the range of 88 up to 98 mol%,
and
b falls in the range of 2 up to 12 mol%.

14. A composition according to claim 1 wherein X is hydrogen,
in the range of 70 up to 85 mol% of the X' groups are -OH, and in the range of 5 up to 25 mol% of the X' groups are -OAc,
n is 0, therefore Y is not present,

Z is -O-,
R" is methyl,
a falls in the range of 88 up to 98 mol%,
and
b falls in the range of 2 up to 12 mol%.

15. A composition according to claim 1 further comprising inhibitors, defoaming agents, surfactants, dyes, ultraviolet light absorbers, plasticizers, lubricating agents, or mixtures of any two or more thereof.

16. A solid water-developable photosensitive resin plate comprising a support having deposited thereon a layer of photopolymerizable composition according to claim 1, wherein said plate is characterized by:

5 producing a sharp image, as determined by the
 method described in Example 2A, after photo-
 polymerization and development thereof,
 producing an image capable of holding 2% dots at
 120 lines per inch, as determined by the
10 highlight dot holding test as described in
 Example 2B, after photo-polymerization and
 development thereof,
 being relatively insensitive to variations in
 processing conditions employed for washout
15 of the photopolymerizable composition, and
 producing a durable printing surface after photo-
 polymerization and development thereof.

17. A plate according to claim 16 wherein said support is selected from metal or plastic material.

18. A plate according to claim 16 further comprising an adhesive layer between said support and said photopolymerizable composition.

19. A plate according to claim 16 further comprising a matte coat on top of the photopolymerizable composition.

20. A plate according to claim 16 wherein said photopolymerizable composition is applied to said support at a thickness of at least 7 mils.

21. A relief printing plate comprising a support having deposited thereon a photopolymerized layer of photopolymerizable composition according to claim 1 at a thickness of at least 7 mils, wherein said plate is
5 characterized by:

producing a sharp image, as determined by the method described in Example 2A, after photopolymerization and development thereof,
10 producing an image capable of holding 2% dots at 120 lines per inch, as determined by the highlight dot holding test as described in Example 2B, after photo-polymerization and development thereof,
15 being relatively insensitive to variations in processing conditions employed for washout of the photopolymerizable composition, and producing a durable printing surface after photopolymerization and development thereof.

22. A method for preparing a water-developable photosensitive resin plate suitable for the manufacture of a printing plate, said method comprising depositing onto a suitable support a substantially homogenous composition
5 according to claim 1, wherein said plate is characterized by:

producing a sharp image, as determined by the method described in Example 2A, after photopolymerization and development thereof,

10 producing an image capable of holding 2% dots at
 120 lines per inch, as determined by the
 highlight dot holding test as described in
 Example 2B, after photo-polymerization and
 development thereof,
15 being relatively insensitive to variations in
 processing conditions employed for washout
 of the photopolymerizable composition, and
 producing a durable printing surface after photo-
 polymerization and development thereof.

23. A method according to claim 22 wherein said
depositing is carried out by extrusion, roll coating, heat
processing or casting.

24. A method for preparing a relief printing
plate, said method comprising:

 exposing a photosensitive resin plate
 according to claim 16, through a negative film
5 having an image thereon, to electromagnetic
 radiation of sufficient energy to promote the
 polymerization of said resin, and
 washing said plate with a sufficient
 quantity of water to remove the photosensitive
10 resin composition from the non-exposed portions
 of said plate,

 wherein said plate is characterized, after
photopolymerization and development thereof, by:

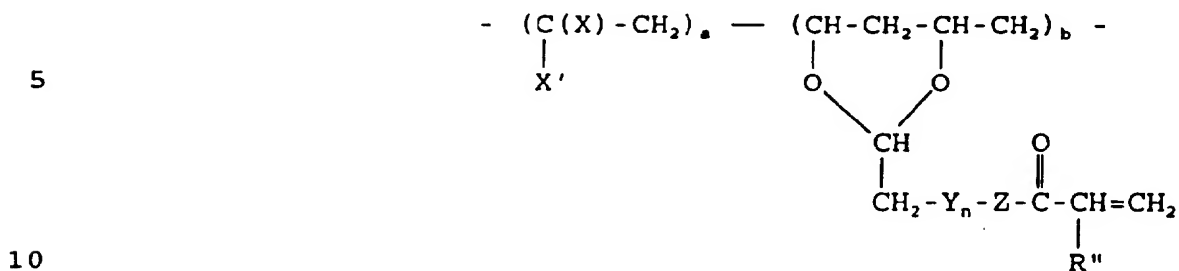
 producing a sharp image, as determined by the
15 method described in Example 2A, after photo-
 polymerization and development thereof,
 producing an image capable of holding 2% dots at
 120 lines per inch, as determined by the
 highlight dot holding test as described in
20 Example 2B, after photo-polymerization and
 development thereof,

being relatively insensitive to variations in processing conditions employed for washout of the photopolymerizable composition, and producing a durable printing surface after photopolymerization and development thereof.

25. A method according to claim 24 wherein the water employed for said washing is applied as a spray or with a brush.

26. The printing plate obtained by the method of claim 25.

27. A method for the preparation of a polyvinyl alcohol (PVA) derivative having the structure:



wherein:

X is hydrogen or $-\text{CO}_2\text{H}$,

15 X' is -OR, wherein each R is independently selected from -H, -CH₂CH₂OH or -C(O)CH₃, when X is hydrogen; or X' is -CH₂CO₂H when X is -CO₂H, with the proviso that at least 55 mol% of the X' groups are -OH;

each Y is independently selected from
20 -CH₂- or -O-CH₂CH₂-;

each Z is independently selected from -O- or -NR'-, wherein each R' is independently selected from H or lower alkyl;

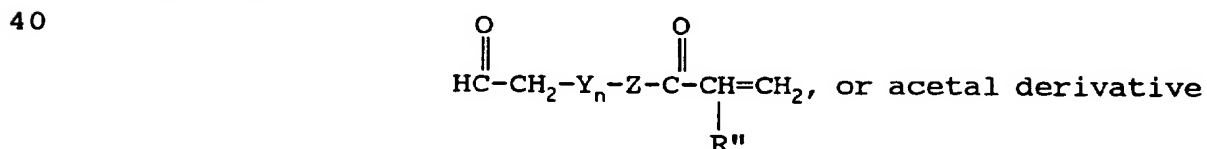
25 each R" is independently selected from
H or lower alkyl;

a falls in the range of about 65 up to
99 mol%, based on the total moles of
monomeric units contained in said PVA
30 derivative; and

b falls in the range of about 1 up to
35 mol%, based on the total moles of
monomeric units contained in said PVA
derivative, and

35 n falls in the range of about 0 up to
8,

said method comprising contacting polyvinyl
alcohol with at least one reactive species having the
structure:



45 thereof, wherein said contacting is carried out in aqueous
medium under condensation conditions.

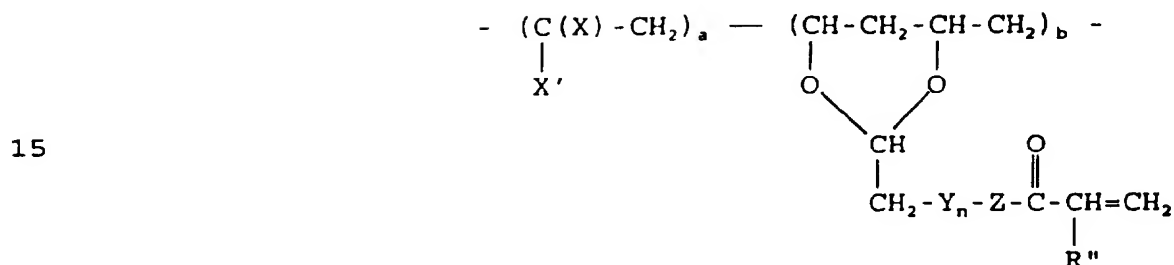
28. A method according to claim 27 wherein
condensation conditions comprise acidic media and mild
heating.

29. A method for the preparation of a
composition according to claim 1, said method comprising
contacting polyvinyl alcohol with at least one reactive
species having the structure:



10 in aqueous medium under conditions suitable to produce a
polyvinyl alcohol (PVA) derivative having the structure:

35



20

wherein:

X is hydrogen or $-\text{CO}_2\text{H}$,

25

X' is $-\text{OR}$, wherein each R is independently selected from $-\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$ or $-\text{C}(\text{O})\text{CH}_3$, when X is hydrogen; or X' is $-\text{CH}_2\text{CO}_2\text{H}$ when X is $-\text{CO}_2\text{H}$, with the proviso that at least 55 mol% of the X' groups are $-\text{OH}$;

30

each Y is independently selected from $-\text{CH}_2-$ or $-\text{O}-\text{CH}_2\text{CH}_2-$;

each Z is independently selected from $-\text{O}-$ or $-\text{NR}'-$, wherein each R' is independently selected from H or lower alkyl;

35

each R'' is independently selected from H or lower alkyl;

40

a falls in the range of about 65 up to 99 mol%, based on the total moles of monomeric units contained in said PVA derivative; and

b falls in the range of about 1 up to 35 mol%, based on the total moles of monomeric units contained in said PVA derivative, and

45

n falls in the range of about 0 up to 8,

and thereafter introducing the desired quantities of ethylenically unsaturated monomer(s) and photoinitiator(s).

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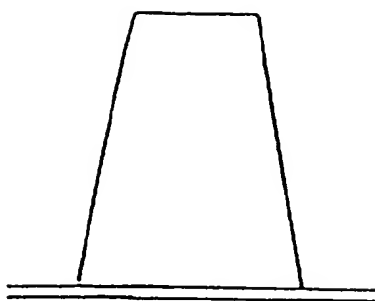


FIGURE 1A

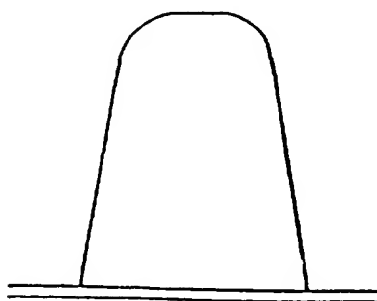


FIGURE 1B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/15036

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G03C 1/00, 1/725, 1/73, 1/735, 5/16; G03F 7/027, 7/038, 7/30

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/18, 281, 287.1, 288.1, 325, 306, 909; 522/85, 114, 116, 117, 120, 121

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
noneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 2,929,710 (MARTIN) 22 March 1960; column 1, lines 15-32; column 2, lines 58-82; column 3, lines 1-20; column 19, line 52, to column 20, line 14; column 20, lines 55-60; column 16, lines 1-6; column 17, line 45, to column 18, line 21; column 21, lines 12-36, and the Examples.	1-29
X --- Y	US, A, 4,517,277 (LYNCH ET AL) 14 May 1985, see the Abstract and the Examples.	1-15 ----- 16-29
Y	EP, A, 1,233,883 (NIPPON PAINT CO.) 03 June 1971, page 5, lines 35-96.	16-26
X	GB 0,834,337 (DU PONT DE NEMOURS AND COMPANY) 13 August 1957, page 3, lines 30-115, pages 4-5 and the Example.	1-29

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 07 FEBRUARY 1996	Date of mailing of the international search report 21 FEB 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer SUSAN BERMAN Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US95/15036**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y Y	US, A, 4,355,093 (HARTMANN ET AL) 19 October 1982, Abstract, column 2, line 30, to column 3, line 31; Example 1. US, A, 4,042,386 (OKAI ET AL) 16 August 1977, column 2, line 34, to column 4, line 3; column 4, lines 48-59.	1-15,27-29 ----- 16-26 1-26

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15036

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

430/18, 281, 287.1, 288.1, 325, 306, 909; 522/85, 114, 116, 117, 120, 121